From:	MCCLINCY Matt
To:	DeMaria, Eva
Subject:	FW: C10-C12 Question
Date:	Tuesday, October 18, 2016 11:33:52 AM

From: Shephard, Burt [mailto:Shephard.Burt@epa.gov]
Sent: Wednesday, December 31, 2014 1:44 PM
To: Muza, Richard; Koch, Kristine
Cc: POULSEN Mike; LARSEN Henning
Subject: RE: C10-C12 Question

Rich,

Short answer, no the Portland Harbor TPH toxicity reference values (TRVs) and preliminary remedial goals (PRGs) are not based on equivalent carbons (EC), despite the implication in Henning's e-mail of December 18th that the TPH PRGs are or should be based on their equivalent carbon value. The TPH ecological TRVs are based on the actual chemical structure of the individual chemicals used to derive the TPH toxicity benchmarks, not the equivalent carbon (EC) value for an individual chemical. Toxicologically, all previous efforts to develop TPH TRVs described in Henning's e-mail are not, indeed cannot be based on EC ranges, for the reasons described in detail below. Unfortunately, there is a disconnect between what the toxicologists/risk assessors need to measure and how analytical chemists define equivalent carbon ranges in their analytical methodologies. The ecotoxicological literature on which the Portland Harbor TPH TRVs are based do not make use of equivalent carbon terminology in the toxicological studies. If you like, I can send PDFs of the actual peer reviewed literature of the toxicity of TPH to aquatic species, and you can do your own search for the phrase 'equivalent carbon'. I've already done it, you won't find 'equivalent carbon' in any of the literature. However, with proper selection of the individual chemicals used to derive TPH fraction toxicity, we can also base TRVs on chemicals that are detected by analytical laboratories within any defined equivalent carbon (EC) range, at least for the lower molecular weight compounds for which we have TRVs at Portland Harbor. Thus, the disconnect between toxicology and analytical chemistry may not be as bad as it first appears, and can be completely eliminated with a little discussion.

Ecological risk toxicity reference values (TRVs), as well as human health risk reference doses and chemical concentrations posing any defined probability of excess lifetime cancer risk, are all described in terms of the concentration of that chemical (or mixture of chemicals) in an environmental medium that elicit a defined level of toxicity. The defined level of toxicity can be a no effect concentration, a lowest observed adverse effect level, a concentration associated with $1x10^{-6}$ lifetime excess cancer risk, etc. For risk assessors to properly evaluate risks from the concentration of a chemical in any medium (water, soil, sediment etc.), the analytical chemistry method used has to be able to quantify the chemical in the medium at a concentration lower than its TRV, reference dose, etc. This is the reason we always compare analytical detection limits to toxicity values in work plans and QAPPs. Toxicologically, TRVs, reference doses etc. are not defined in terms of what an analytical method detects, nor are they defined on what chemical form an analytical method detects. The opposite is true. An analytical method has to be able to detect the toxicologically active chemical(s) in a medium. This difference between what analytical methods detect and what toxicologists need to measure must be remembered when discussing toxicity

expressed in carbon ranges.

Carbon ranges can be defined by one of two methods: the equivalent carbon (EC) approach and the actual number of carbons/molecule approach. The equivalent carbon range (EC) is based on the boiling point of individual compounds in petroleum mixtures. It is defined by the retention time of the compounds in a gas chromatograph column, normalized to the n-alkanes. Thus, for normal alkanes, the EC and actual number of carbons are identical: n-hexane, with 6 carbon atoms, also has an EC of 6.0, n-dodecane with 12 carbon atoms has an EC of 12.0, etc. The EC method groups chemicals into environmental fate and transport fractions. Furthermore, this is typically how analytical methods identify individual chemicals in a mixture (by retention time, which gets longer as the boiling point increases in a gas chromatograph column). Analytical labs generally report TPH fractions as carbon number ranges by EC groups. Oregon's TPH fractions in their regulations are defined as EC ranges for a series of aliphatic and aromatic groups. The disparity between actual and equivalent carbon numbers is greater for aromatics than aliphatic TPH constituents, and increases with increasing carbon numbers (i.e. ethylbenzene has 8 carbons, but an EC of 8.5, while chrysene has 18 carbons but an EC of 27.41). The EC approach is useful for grouping TPH components into chemicals with similar environmental fate and transport properties.

The toxicity of individual chemicals within TPH mixtures, however, is not based or dependent on the boiling point of the individual chemicals. Therefore, an EC grouping tells you nothing about the toxicity of chemicals within that group. All empirical toxicity data on individual chemicals within TPH mixtures are based on the molar concentration of the individual chemical in the tissues of the ecological receptor. One mole of a substance has 6.02×10^{23} molecules (Avogadro's number). The uptake (bioaccumulation) of the individual chemicals is not determined by the boiling point of the compound. For aquatic species (indeed for all species where a chemical elicits toxicity via a narcosis mode of action, the case for petroleum compounds), the concentration of an individual TPH component in tissue that is lethal to the species is fairly constant, between 2 – 8 millimoles/kilogram body weight (mmol/kg). The chronic (long-term exposure) no effect concentration in tissues of aquatic species is about 10% of the lethal body burden. We used 0.24 mmol/kg as the chronic NOEC for the Portland Harbor TPH benchmark derivation based on measured adverse effect and no effect tissue residues in aquatic species from the literature.

The process works for TPH mixtures because all of the individual chemicals in TPH require the same 2 – 8 mmol/kg in tissue to cause mortality, and their toxicity is additive. That means if one had two chemicals in a TPH mixture at the same concentration, the concentration in tissue of each of the two chemicals would be 1 – 4 mmol/kg. Individually, the two chemicals might not be lethal. But adding their molar concentrations together gives you the 2 – 8 mmol/kg lethal body burden. For 10 chemicals in a mixture at equal concentrations, each of the 10 chemicals having a concentration in tissue of 0.2 – 0.8 mmol/kg results in a sum of 2 – 8 mmol/kg, the lethal body burden, and so on. This additive toxicity feature is how we can calculate the toxicity of a TPH mixture of any composition to aquatic species. To obtain the water TRV, we simply have to run a bioaccumulation model backwards to solve for the water concentration that results in a total of no more than 0.24 mmol/kg TPH in the tissues of aquatic species. Because petroleum is a mixture of hundreds of individual compounds, toxicologists, like analytical chemists, break total TPH mixtures into a number of fractions, use one or more surrogate compounds within that fraction to represent the

concentration and toxicity of all chemicals within that fraction, then sum the molar concentration of the surrogates to determine whether or not the bioaccumulated TPH concentration is high enough to elicit toxicity. This surrogate chemical approach saves us from having to define the concentration and toxicity of each chemical within a TPH mixture.

All toxicity data, both ecological and human health, is based on the actual composition and structure of the chemical, not its equivalent carbon number. This is true for all efforts that have tried to derive and publish TPH environmental quality benchmarks, reference doses for human health risks, toxicity reference values, etc., including those that Henning mentions in his attached e-mail message. In summary, toxicologists and risk assessors describe TPH toxic concentrations in terms of the actual chemical structure and number of carbons in a chemical, analytical chemists describe TPH concentrations in terms of boiling point ranges for chemicals. This is the difference that needs to be resolved so that TPH TRVs (or PRGs in the Portland Harbor FS) and measured TPH fractions in environmental samples align with each other. To align with analytical chemistry methods, which describe concentrations in multiple TPH fractions, such as Oregon's 7 aliphatic fractions and 5 aromatic fractions, toxicologists pick one or more surrogate chemicals for which empirical toxicity data are available, use them as surrogates for or representatives of all chemicals within that TPH fraction, and derive toxicity benchmarks for each TPH fraction using the procedures described in the previous paragraph. Analytical measurement should detect the chemical(s) on which toxicity is based. Toxic chemical concentrations in environmental samples cannot be forced into fitting within a range of chemicals a chemist can measure. As a lawyer would say, the toxic concentrations are what they are, they are not what a chemist says they can measure.

For ethylbenzene, the surrogate aromatic compound for the Oregon C8 – C10 aromatic fraction, it's no effect concentration in tissue is based on the molar concentration of 0.24 mmol/kg in tissue. Given ethylbenzene's molecular formula of C_8H_{10}, its molecular weight is 106.2. One mole of ethylbenzene thus weighs 106.2 grams, one millimole ethylbenzene weigh 0.1062 grams (106.2 milligrams), and 0.24 millimole ethylbenzene weighs 0.24 x 106.2 mg = 25.5 mg. This means an ethylbenzene no effect tissue residue of 0.24 mmol/kg is equivalent to a ethylbenzene concentration in tissue of 25.5 mg/kg. Ethlybenzene's equivalent carbon (EC) value is 8.5. However, this does not mean that ethylbenzene has the chemical formula of $C_{8.5}H_{10}$, nor does it mean ethylbenzene's molecular weight is 112.2 instead of 106.2, or that 0.24 mmol ethylbenzene weighs 26.9 mg instead of 25.5 mg. Toxicity is based on the actual chemical structure of the compound, not its equivalent carbon boiling point.

Having said all of the above, as long as the surrogate compound describing toxicity of a range of chemicals also has an EC that falls within the range of EC described in Oregon's definition of TPH fractions, the toxicological surrogate will be analyzed within that EC fraction reported by a laboratory. When this is the case, the toxicological carbon range aligns with the EC range of Oregon's TPH regulations. Thus, there is no conflict between the needs of the risk assessor and what a chemist can measure in this situation. I'll break down the situation with the Portland Harbor TPH TRVs and Oregon's defined TPH fractions into discussion of aliphatics and aromatics separately

Since EC's are normalized to the boiling point and retention time on a GC column of n-alkanes, and we used n-alkanes for surrogates in all of the derivations of TRVs for aliphatics at Portland Harbor,

all toxicity reference values for aliphatics will represent the toxicity of the EC fraction defined by Oregon. The specific details are in the table below.

Oregon aliphatic fraction	Toxicological surrogate for fraction	Actual number of carbons	Equivalent carbon number
C5 – C6	n-hexane	6	6
C6 – C8	n-heptane	7	7
C8 – C10	n-nonane	9	9
C10 – C12	n-undecane	11	11

No problems for the aliphatics, the toxicological surrogates are all detected within the equivalent carbon range described in the Oregon regulations, thus they are in alignment.

For aromatics, where we used ethylbenzene with an EC of 8.5 as the surrogate aromatic for the Oregon C8 – C10 aromatic fraction, the toxicity reference value also lines up with the analytical method. This is not the case for the Oregon C10 – C12 aromatic fraction, where toxicologically we used 2-methylnaphthalene with 11 carbon atoms ($C_{11}H_{10}$), with a molecular weight of 142.2 as the toxicological surrogate for the C10 – C12 aromatic fraction. However, the equivalent carbon value for 2-methylnaphthalene is 12.84, analytically placing it within Oregon's C12 – C16 aromatic EC fraction, as shown in the table below. This equivalent carbon value would imply 2-methylnaphthalene has a molecular weight of 164.3, not its actual molecular weight of 142.2. This difference when extended into the TPH TRV derivation yields a no effect tissue residue of 39.4 mg/kg 2-methylnaphthalene, instead of its actual no effect tissue residue of 34.1 mg/kg.

Oregon aromatic fraction	Toxicological surrogate for fraction	Actual number of carbons	Equivalent carbon number
C8 – C10	Ethylbenzene	8	8.50
C10 – C12	2-methylnaphthalene	11	12.84

Toxicologically, 2-methylnaphthalene fits into the aromatic C10 – C12 fraction. However, based on its equivalent carbon value of 12.84, 2-methylnaphthalene fits into the aromatic C12 – C16 equivalent carbon fraction. Presumably bioaccumulation of a higher no effect tissue residue would require a higher chemical concentration in water, since bioaccumulation is not dependent on the boiling point or equivalent carbon number of a chemical (bioaccumulation is better described by the value of the log octanol-water partition coefficient of a chemical).

This leaves us with one of two possibilities: 1) get an analytical method that measures 2-methylnaphthalene as part of the actual C10 – C12 fraction, as opposed to in the EC C12 – C16 fraction, or 2) find a different aromatic surrogate chemical with both actual and EC carbon values between C10 and C12, then recalculate the TRV. I'm aware of two such aromatics, although I'm sure there are others. The two are:

Naphthalene (actual C10, EC = 11.69)
n-butylbenzene (actual C10, EC = 10.50)

I'm unaware of any empirical toxicity data for n-butylbenzene. There is empirical toxicity data for naphthalene (as there is for 2-methylnaphthalene), but naphthalene also exhibits photoinduced toxicity when exposed to UV light (i.e. sunlight) in addition to its narcosis mode of action, making naphthalene a less than ideal surrogate compound.

Again, I have to reiterate, it's the job of the analytical chemists to detect the chemicals that elicit toxicity to ecological receptors. It is not the job of the risk assessors to change a toxicity reference value just because the analytical chemists have a problem detecting the chemical causing the toxicity, or it doesn't fit within the preconceived notion of how a chemist measures a chemical, when that preconceived notion has no relationship to the toxicity of the chemical. Somebody was able to detect 2-methylnaphthalene in environmental samples, otherwise empirical toxicity data for it would not exist.

Best regards,

Burt Shephard
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"Facts are stubborn things"
- John Adams

From: Muza, Richard
Sent: Monday, December 22, 2014 6:35 AM
To: Koch, Kristine; Shephard, Burt
Subject: FW: C10-C12 Question

Kristine & Burt

Hi. Please see note below and let me know if Henning's assumption is correct. THANKS!

Rich

Rich Muza
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From: LARSEN Henning [mailto:LARSEN.Henning@deq.state.or.us]
Sent: Thursday, December 18, 2014 3:06 PM
To: Muza, Richard
Cc: MCCLINCY Matt
Subject: RE: C10-C12 Question

Rich, I want to ask you one last clarifying question on the C10-C12 aliphatic & aromatic hydrocarbon PRGs for the Portland Harbor project. Can you confirm the TPH fraction PRGs developed by EPA are based on "Equivalent Carbons" (**EC10-EC12**) ? This is the typical way TPH fractions are defined (State MA, State of OR, NWTPH VPH and EPH analytical methods, TPH working Group etc.), however I didn't see where that was explicitly stated. If they are based on equivalent carbon, than our VPH/EPH analytical methods sync up with the PRGs, exactly. Thanks.

Have a great Holiday.

Henning

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From: Muza, Richard [mailto:Muza.Richard@epa.gov]
Sent: Thursday, December 04, 2014 10:53 AM
To: MCCLINCY Matt
Cc: HARMAN Charles; LARSEN Henning
Subject: RE: C10-C12 Question

Matt

Hi. I did get feedback on this question. Yes, the proposed PRG is inclusive of C10, C11, and C12 aromatic and aliphatic hydrocarbons. I'm working on getting answers to the questions in Tom Graf's email.

THANKS!

Rich

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From: MCCLINCY Matt [mailto:MCCLINCY.Matt@deq.state.or.us]
Sent: Tuesday, December 02, 2014 11:42 AM
To: Muza, Richard
Cc: harman.charles@deq.state.or.us; LARSEN Henning
Subject: RE:C10-C12 Question

Hey Rich,

See the question below from Henning. Can you coordinate at your end? This question is in addition to the questions that Patrick Hubbard is putting together.

Thanks,

Matt McClincy

From: LARSEN Henning
Sent: Tuesday, December 02, 2014 11:06 AM
To: HARMAN Charles; MCCLINCY Matt
Subject: Follow-Up to Yesterday's Meeting

Chuck/Matt – Patrick Hubbard asked "***How is the C10-C12 range defined'*** I indicated it included both aromatic and aliphatic compounds and ranged from C10-C12 and that those fractions aligned with our VPH and EPH analyses and the ranges they quantify. However, upon closer examination this response is not completely accurate. Rich Musa sent me an Excel table of PH PRGs in March 2014 and the fractions described in it are "***TPH (C-10 to C-12 aliphatic/aromatic)"*** - inclusive of C10 range hydrocarbons. Whereas, this excerpt from the description of the EPH analytical method developed by Washington State

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indicates the analytical method quantifies C8 - C10 and >C10 – C12; the second fraction does not include C10 while the PRG does . So it would appear the PH PRG fractions do not exactly coincide with the fractions quantified by our VPH/EPH methods. If true, this is a bit of a wrinkle for a lot of sites and might require a significant modification of the analytical method. Could either of you get clarification from EPA that that is what they intended (aromatic and aliphatic C10-C12 inclusive of C10 hydrocarbons).

Henning

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